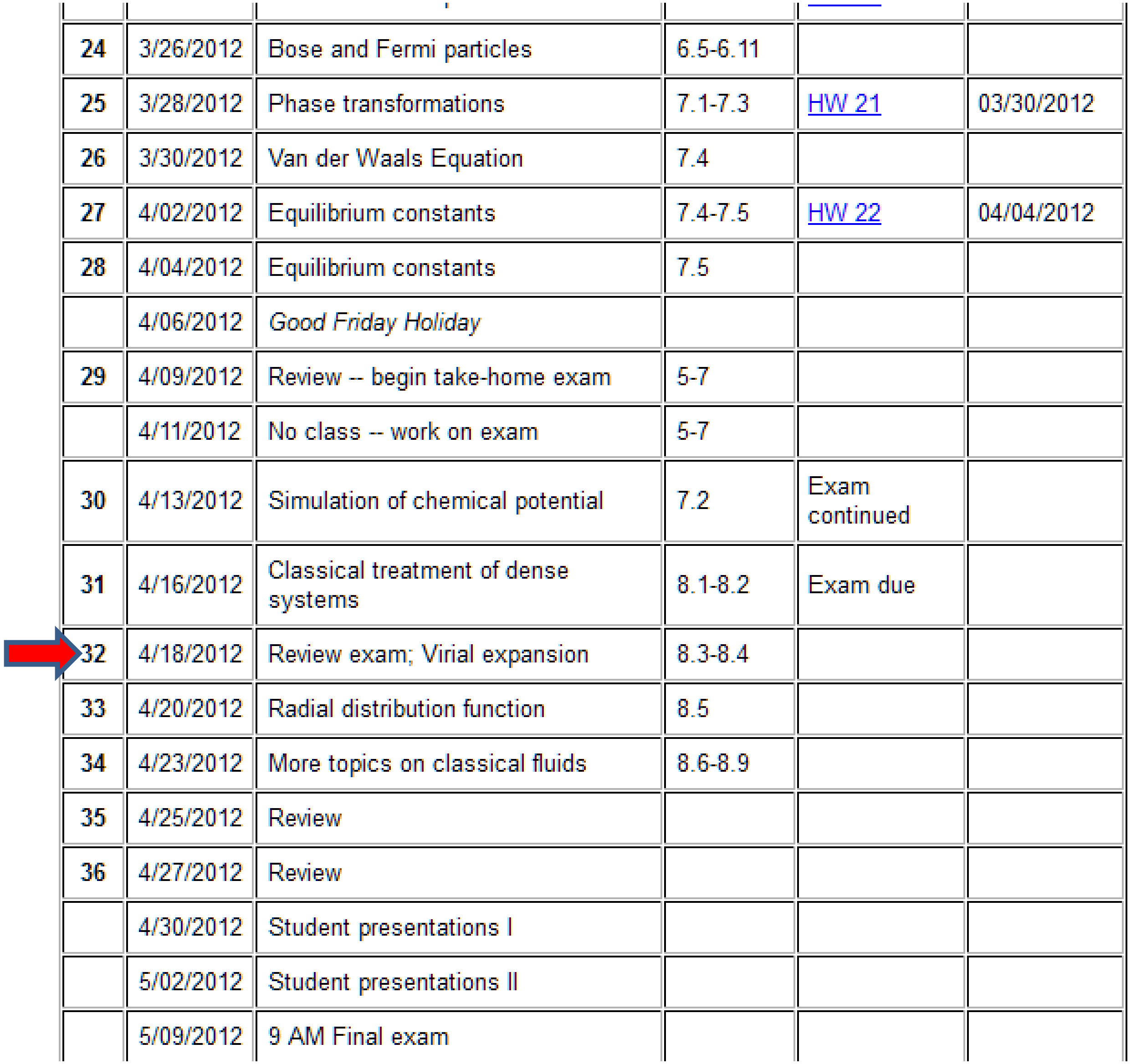
PHY 341/641
Thermodynamics and Statistical Physics

Lecture 32

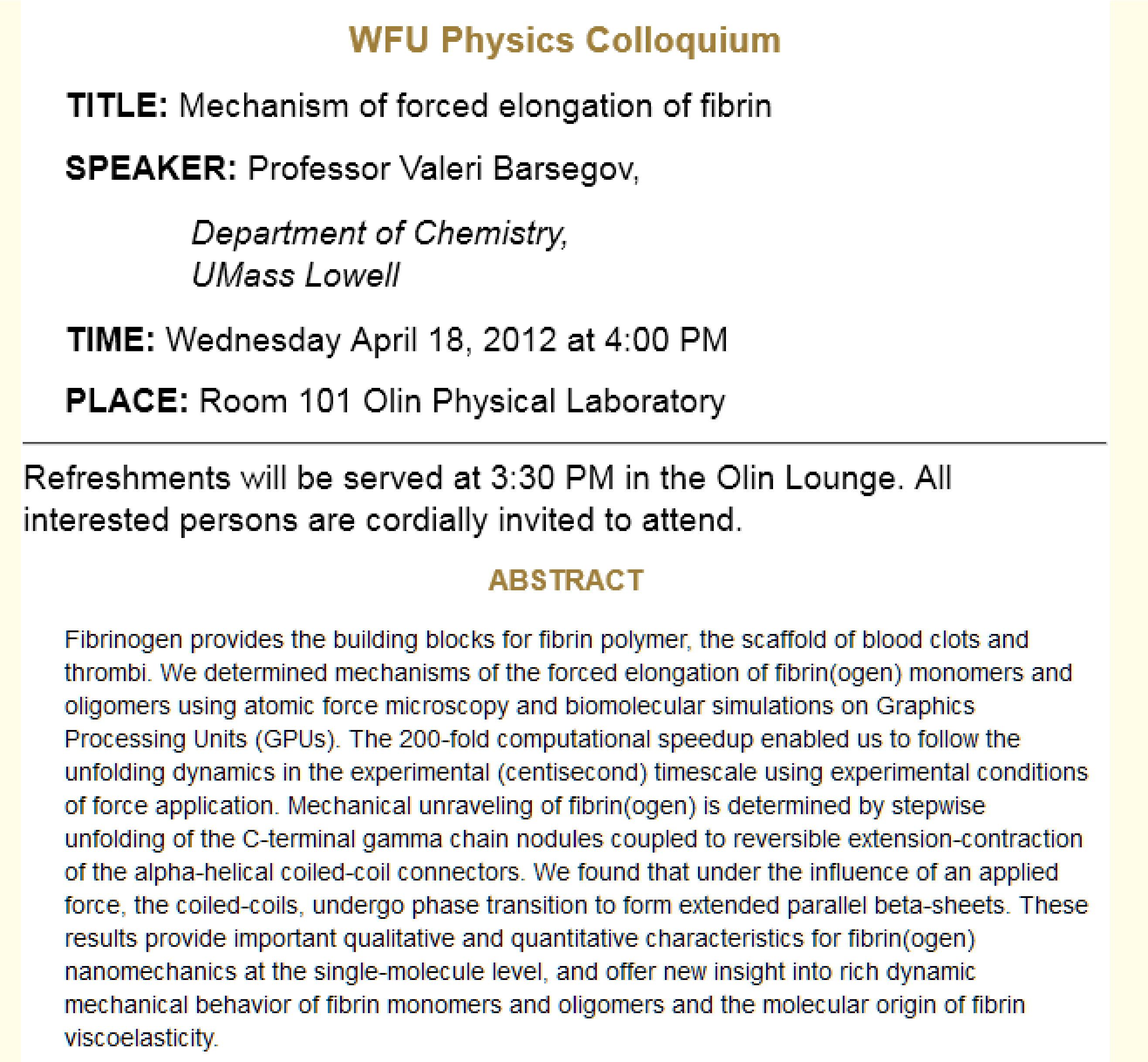
Analysis of classical gases and liquids (STP Chapt. 8)

- Comments about exam
- Virial coefficients
- Radial distribution functions



24	3/26/2012	Bose and Fermi particles	6.5-6.11		
25	3/28/2012	Phase transformations	7.1-7.3	HW 21	03/30/2012
26	3/30/2012	Van der Waals Equation	7.4		
27	4/02/2012	Equilibrium constants	7.4-7.5	HW 22	04/04/2012
28	4/04/2012	Equilibrium constants	7.5		
	4/06/2012	*Good Friday Holiday*			
29	4/09/2012	Review -- begin take-home exam	5-7		
	4/11/2012	No class -- work on exam	5-7		
30	4/13/2012	Simulation of chemical potential	7.2	Exam continued	
31	4/16/2012	Classical treatment of dense systems	8.1-8.2	Exam due	
32	4/18/2012	Review exam; Virial expansion	8.3-8.4		
33	4/20/2012	Radial distribution function	8.5		
34	4/23/2012	More topics on classical fluids	8.6-8.9		
35	4/25/2012	Review			
36	4/27/2012	Review			
	4/30/2012	Student presentations I			
	5/02/2012	Student presentations II			
	5/09/2012	9 AM Final exam			

-- student presentations 4/30, 5/2 (need to pick topics)



WFU Physics Colloquium

TITLE: Mechanism of forced elongation of fibrin

SPEAKER: Professor Valeri Barsegov,

Department of Chemistry,
UMass Lowell

TIME: Wednesday April 18, 2012 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

Fibrinogen provides the building blocks for fibrin polymer, the scaffold of blood clots and thrombi. We determined mechanisms of the forced elongation of fibrin(ogen) monomers and oligomers using atomic force microscopy and biomolecular simulations on Graphics Processing Units (GPUs). The 200-fold computational speedup enabled us to follow the unfolding dynamics in the experimental (centisecond) timescale using experimental conditions of force application. Mechanical unraveling of fibrin(ogen) is determined by stepwise unfolding of the C-terminal gamma chain nodules coupled to reversible extension-contraction of the alpha-helical coiled-coil connectors. We found that under the influence of an applied force, the coiled-coils, undergo phase transition to form extended parallel beta-sheets. These results provide important qualitative and quantitative characteristics for fibrin(ogen) nanomechanics at the single-molecule level, and offer new insight into rich dynamic mechanical behavior of fibrin monomers and oligomers and the molecular origin of fibrin viscoelasticity.

Time, Einstein, and the Coolest Stuff in the Universe

A free public lecture by Nobel Laureate

Dr. William Phillips

National Institute of Standards and Technology

8:00 PM Friday, April 20

Brendle Recital Hall
Wake Forest University

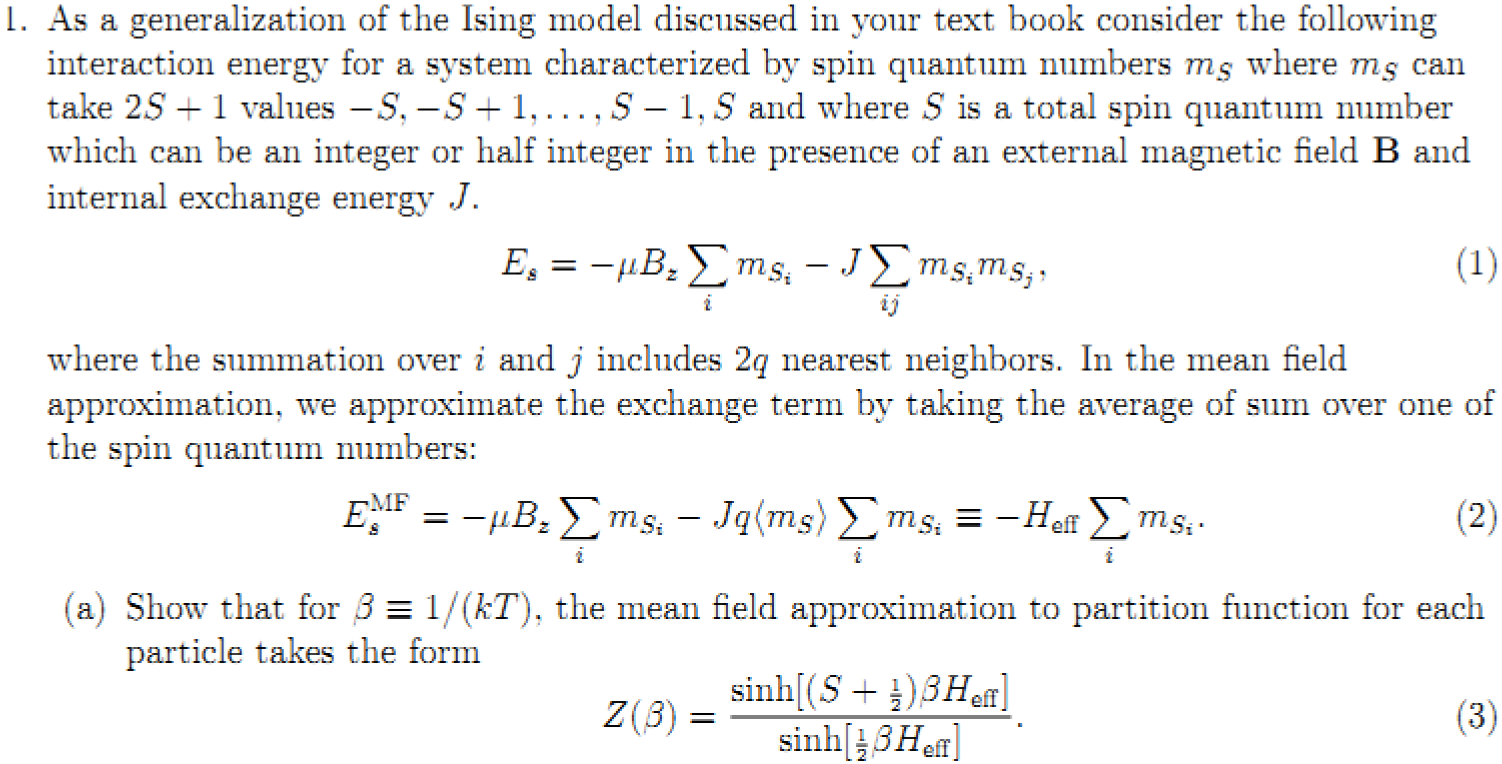
Part of SPS zone 5 conference
April 20-21, 2012

Received 1997 Nobel Prize with Steven Chu and Claude Cohen-Tannoudji “for development of methods to cool and trap atoms with laser light”

www.wfu.edu/physics/sps/spszone52012conf/welcome.html

Suggestions for efficient learning of topics covered on exam

A. Let it stand as is
B. Redo exam – turn in work to count points in HW grade
C. Redo exam – meet with instructor to discuss remaining issues (grading points to be determined)
D. Other??



1. As a generalization of the Ising model discussed in your text book consider the following interaction energy for a system characterized by spin quantum numbers m_S where m_S can take $2S+1$ values $-S, -S+1, \ldots, S-1, S$ and where S is a total spin quantum number which can be an integer or half integer in the presence of an external magnetic field $\mathbf{B}$ and internal exchange energy J.

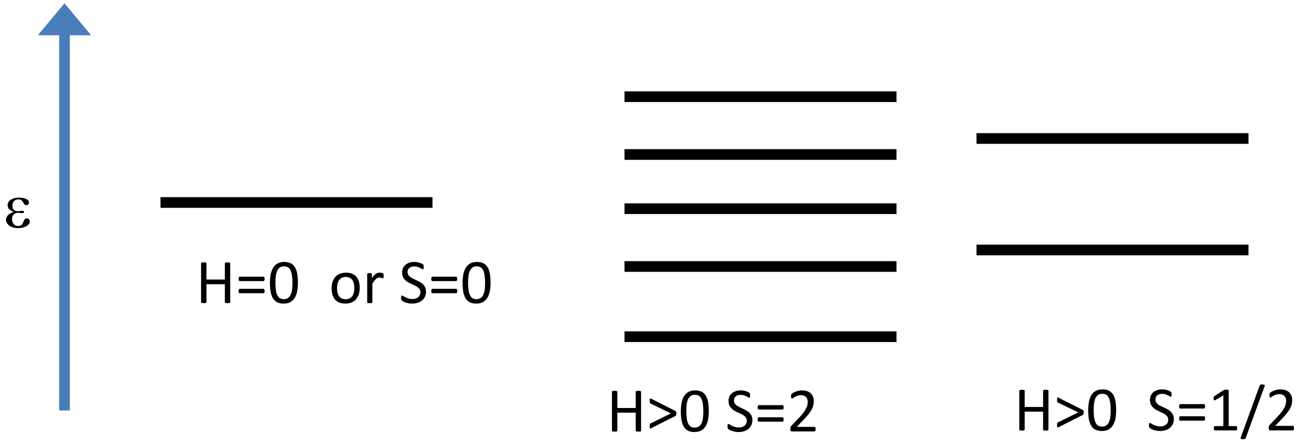
$$E_s = -\mu B_z \sum_i m_{S_i} - J \sum_{ij} m_{S_i} m_{S_j}, \tag{1}$$

where the summation over i and j includes $2q$ nearest neighbors. In the mean field approximation, we approximate the exchange term by taking the average of sum over one of the spin quantum numbers:

$$E_s^{\mathrm{MF}} = -\mu B_z \sum_i m_{S_i} - Jq\langle m_S \rangle \sum_i m_{S_i} \equiv -H_{\mathrm{eff}} \sum_i m_{S_i}. \tag{2}$$

(a) Show that for $\beta \equiv 1/(kT)$, the mean field approximation to partition function for each particle takes the form

$$Z(\beta) = \frac{\sinh[(S+\frac{1}{2})\beta H_{\mathrm{eff}}]}{\sinh[\frac{1}{2}\beta H_{\mathrm{eff}}]}. \tag{3}$$



Hint for finding single particle partition function

$$Z = \sum_{m_S=-S}^{S} e^{-\beta m_S H_{eff}} = e^{\beta S H_{eff}} + e^{\beta(S-1)H_{eff}} + \cdots e^{-\beta(S-1)H_{eff}} + e^{-\beta S H_{eff}}$$

$$= e^{\beta S H_{eff}} \left(\sum_{n=0}^{2S} e^{-\beta n H_{eff}} \right)$$

How to sum geometric series:

$$R \equiv \sum_{n=0}^{M} u^n \qquad \text{Note that:} \quad uR = R - 1 + u^{M+1}$$

$$\Rightarrow \boxed{R = \frac{1-u^{M+1}}{1-u}}$$

Hint for Problem 1 continued:

(a) Show that for $\beta \equiv 1/(kT)$, the mean field approximation to partition function for each particle takes the form

$$Z(\beta) = \frac{\sinh[(S+\frac{1}{2})\beta H_{\text{eff}}]}{\sinh[\frac{1}{2}\beta H_{\text{eff}}]}. \tag{3}$$

(b) Show that the average spin for this system is given by

$$\langle m_S \rangle = S f(\beta H_{\text{eff}}) \tag{4}$$

where

$$f(x) \equiv \frac{1}{S}\left[(S+\tfrac{1}{2})\coth[(S+\tfrac{1}{2})x] - \tfrac{1}{2}\coth[\tfrac{1}{2}x]\right]. \tag{5}$$

$$\langle m_S \rangle = \frac{\sum_{m_S=-S}^{S} m_S e^{-\beta m_S H_{eff}}}{\sum_{m_S=-S}^{S} e^{-\beta m_S H_{eff}}} = -\frac{1}{H_{eff}}\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{H_{eff} Z}\frac{\partial Z}{\partial \beta}$$

Hint for Problem 1 continued:

(c) Show that the self-consistency condition is

$$H_{\text{eff}} = \mu B_z + JqSf(\beta H_{\text{eff}}). \tag{6}$$

(d) Write the corresponding transcendental equation in terms of x and the other parameters of the problem. For certain values of the parameters, this transcendental equation may have solutions in addition to $x = 0$. For small values of x, show that

$$f(x) \approx Kx, \tag{7}$$

and find the expression for the coefficient K.

Note that :

$$\beta H_{eff} = \beta\mu B_z + \beta JqSf\left(\beta H_{eff}\right)$$

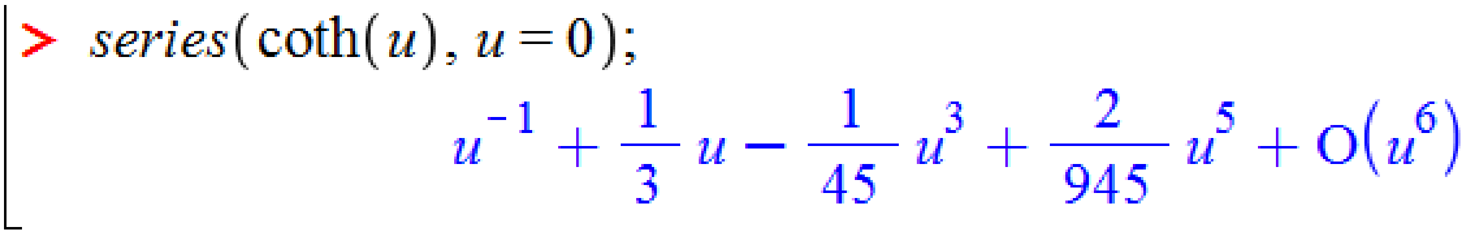
For $x \equiv \beta H_{eff}$: $\qquad x = \beta\mu B_z + \beta JqSf(x)$

Now if $f(x) = Kx$, then self-consistency condition becomes :

$$x = \beta H_{eff} = \frac{\beta\mu B_z}{1 - \beta JqSK}$$

Hint for Problem 1 continued:

$$f(x) \equiv \frac{1}{S}\left[(S+\tfrac{1}{2})\coth[(S+\tfrac{1}{2})x] - \tfrac{1}{2}\coth[\tfrac{1}{2}x]\right].$$



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> series(coth(u), u=0);
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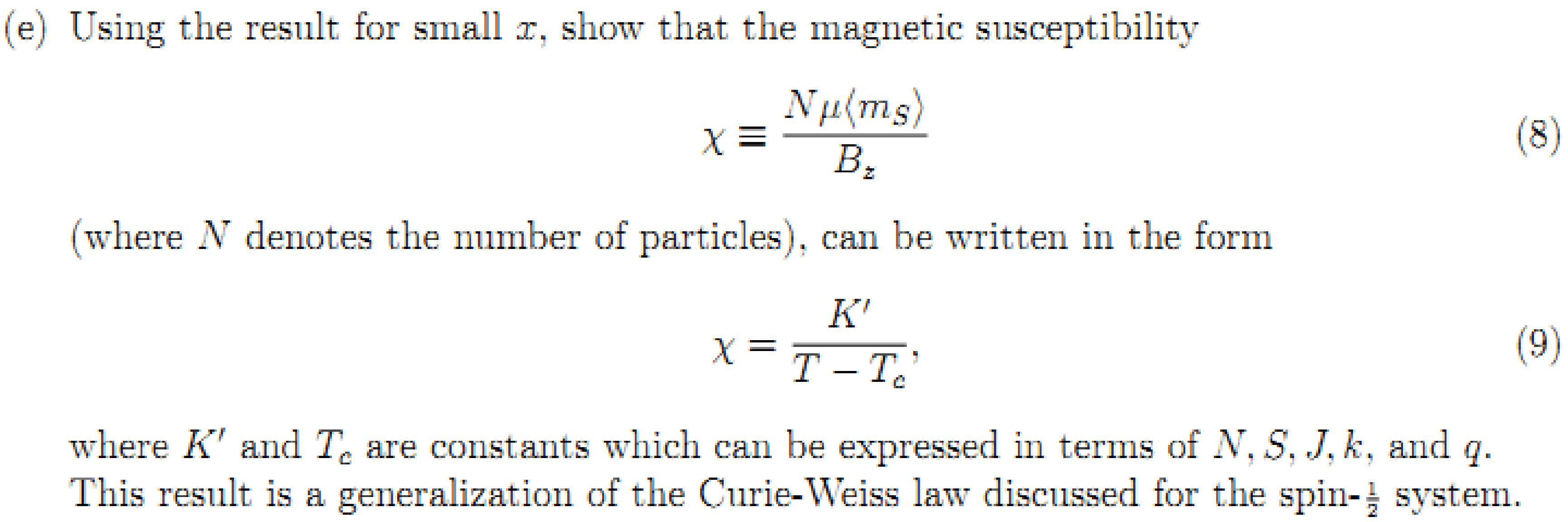
$$u^{-1} + \frac{1}{3}u - \frac{1}{45}u^3 + \frac{2}{945}u^5 + \mathrm{O}(u^6)$$

$$f(x) \xrightarrow[x\to 0]{} \frac{A}{x} + Bx + Cx^3$$

$$\text{If } A \equiv 0, \text{ then } B \equiv K$$

Hint for Problem 1 continued:



(e) Using the result for small x, show that the magnetic susceptibility

$$\chi \equiv \frac{N\mu\langle m_S\rangle}{B_z} \tag{8}$$

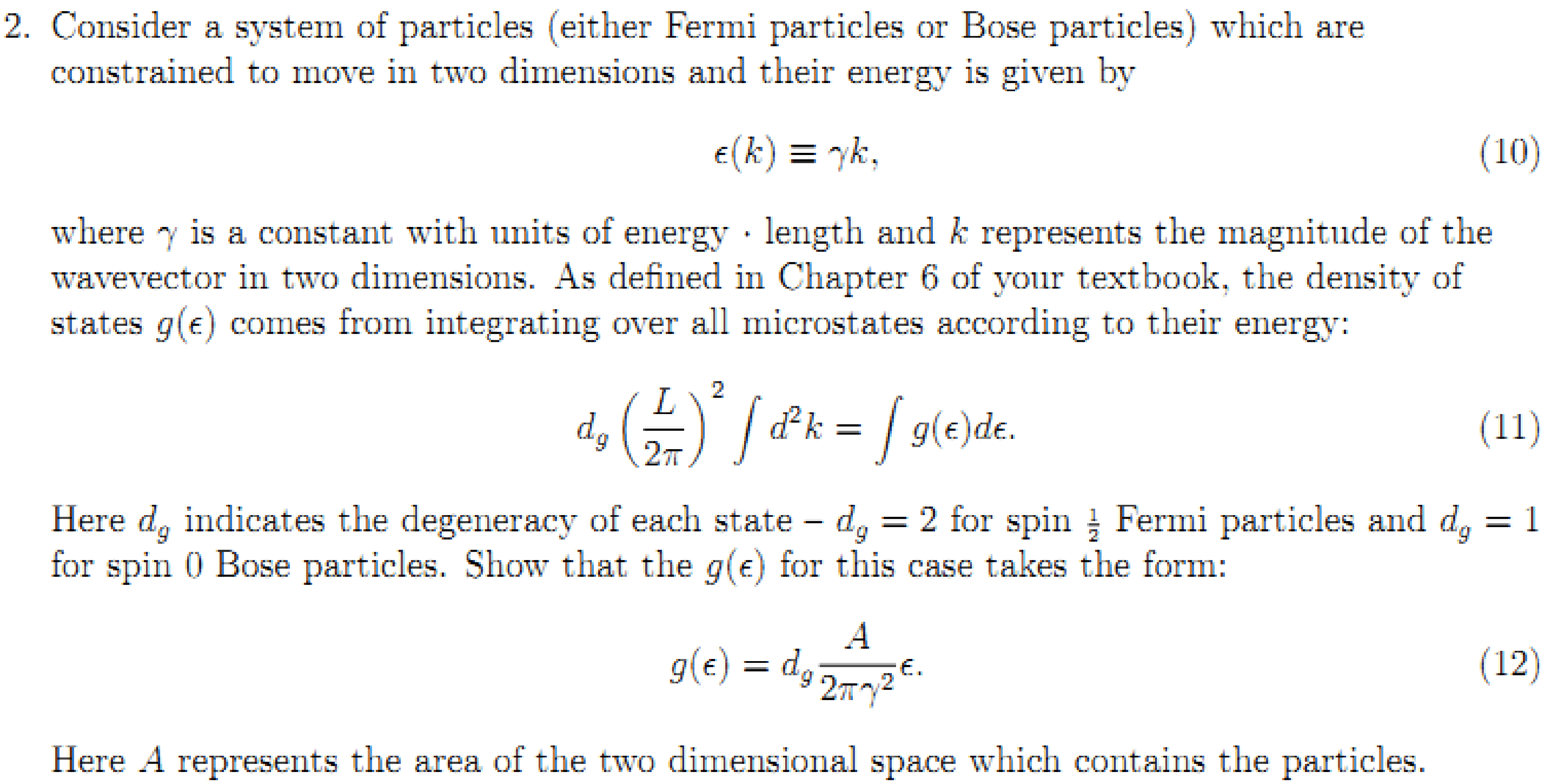
(where N denotes the number of particles), can be written in the form

$$\chi = \frac{K'}{T - T_c}, \tag{9}$$

where K' and T_c are constants which can be expressed in terms of N, S, J, k, and q. This result is a generalization of the Curie-Weiss law discussed for the spin-$\frac{1}{2}$ system.

Note that from previous results :

$$\langle m_S\rangle = Sf\left(\beta H_{eff}\right) \approx SK\beta H_{eff} = SK\frac{\beta\mu B_z}{1-\beta JqSK}$$



2. Consider a system of particles (either Fermi particles or Bose particles) which are constrained to move in two dimensions and their energy is given by

$$\epsilon(k) \equiv \gamma k, \tag{10}$$

where γ is a constant with units of energy · length and k represents the magnitude of the wavevector in two dimensions. As defined in Chapter 6 of your textbook, the density of states $g(\epsilon)$ comes from integrating over all microstates according to their energy:

$$d_g \left(\frac{L}{2\pi}\right)^2 \int d^2k = \int g(\epsilon) d\epsilon. \tag{11}$$

Here d_g indicates the degeneracy of each state – $d_g = 2$ for spin $\frac{1}{2}$ Fermi particles and $d_g = 1$ for spin 0 Bose particles. Show that the $g(\epsilon)$ for this case takes the form:

$$g(\epsilon) = d_g \frac{A}{2\pi\gamma^2} \epsilon. \tag{12}$$

Here A represents the area of the two dimensional space which contains the particles.

Note for isotropic 2-dimensional system: $\int d^2k = 2\pi \int k\,dk = 2\pi \int k \frac{dk}{d\varepsilon} d\varepsilon$

Also note that: $L^2 \equiv A$

3. Now consider the system described in question #2 with N independent spin $\frac{1}{2}$ Fermi particles.

   (a) When the system is at $T = 0K$, find an expression for the chemical potential expressed as a function of N/A.

   (b) In the limit of low temperature ($T > 0K$) find an expression for the heat capacity.

General condition (Chapt. 6 of STP and Lectures 22 - 23) :

$$N = \sum_k \langle n_k \rangle = \int_0^\infty \langle n_\varepsilon \rangle g(\varepsilon) d\varepsilon$$

For Fermi system : $\langle n_\varepsilon \rangle = \dfrac{1}{e^{\beta(\varepsilon-\mu)}+1}$

For $T \to 0$: $\langle n_\varepsilon \rangle \approx \begin{cases} 1 & \text{for } \varepsilon < \mu \\ 0 & \text{for } \varepsilon > \mu \end{cases}$

$$\Rightarrow N \approx \int_0^\mu g(\varepsilon) d\varepsilon$$

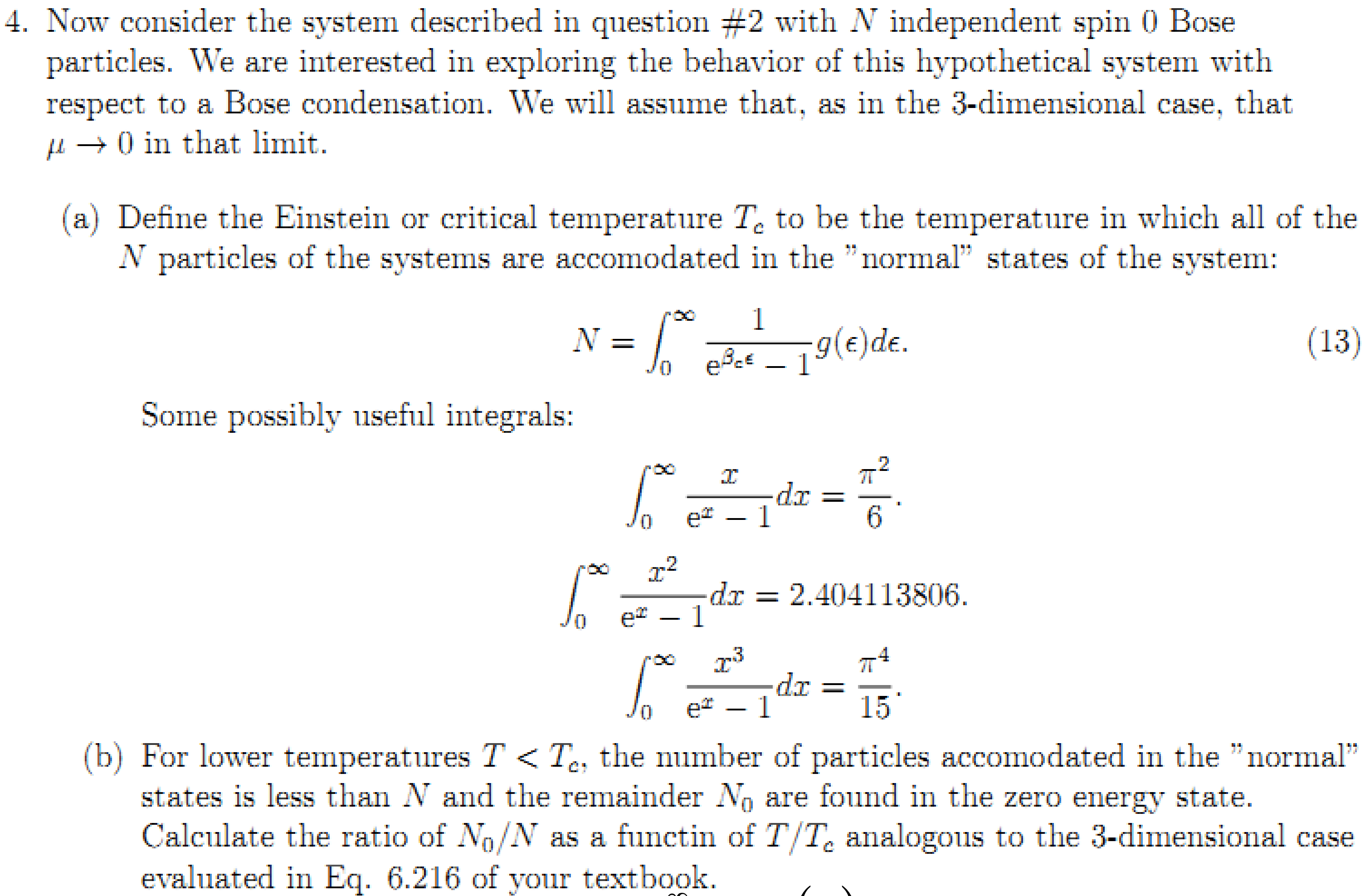
Hint for #3 continued:

$$C_V = \frac{\partial\langle E\rangle}{\partial T} = \frac{\partial}{\partial T}\int_0^\infty \frac{\varepsilon g(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1}d\varepsilon$$

$$= -\frac{1}{kT^2}\int_0^\infty \frac{\partial}{\partial\beta}\left(\frac{1}{e^{\beta(\varepsilon-\mu)}+1}\right)\varepsilon g(\varepsilon)d\varepsilon$$

$$= k\int_{-\beta\mu}^{\infty} \frac{xe^x}{\left(e^x+1\right)^2}\left(\frac{x}{\beta}+\mu\right)g\left(\frac{x}{\beta}+\mu\right)dx$$

$$\text{Note that}: \int_{-\infty}^{\infty} \frac{x^n e^x}{\left(e^x+1\right)^2}dx = \begin{cases} 0 \quad \text{for } n=1 \\ \dfrac{\pi^2}{3} \quad \text{for } n=2 \\ 0 \quad \text{for } n=3 \end{cases}$$



4. Now consider the system described in question #2 with N independent spin 0 Bose particles. We are interested in exploring the behavior of this hypothetical system with respect to a Bose condensation. We will assume that, as in the 3-dimensional case, that $\mu \to 0$ in that limit.

   (a) Define the Einstein or critical temperature T_c to be the temperature in which all of the N particles of the systems are accomodated in the "normal" states of the system:

$$N = \int_0^\infty \frac{1}{e^{\beta_c \epsilon} - 1} g(\epsilon) d\epsilon. \tag{13}$$

   Some possibly useful integrals:

$$\int_0^\infty \frac{x}{e^x - 1} dx = \frac{\pi^2}{6}.$$

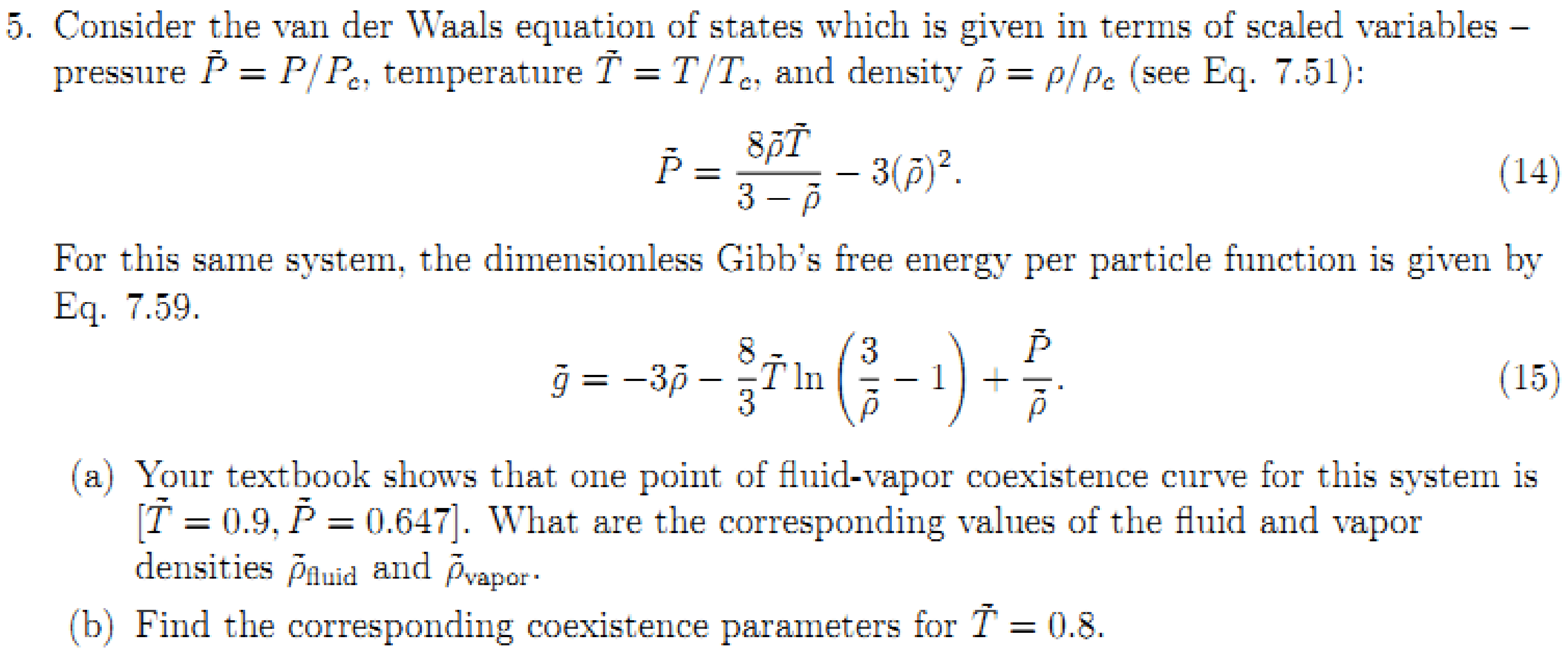
$$\int_0^\infty \frac{x^2}{e^x - 1} dx = 2.404113806.$$

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}.$$

   (b) For lower temperatures $T < T_c$, the number of particles accomodated in the "normal" states is less than N and the remainder N_0 are found in the zero energy state. Calculate the ratio of N_0/N as a functin of T/T_c analogous to the 3-dimensional case evaluated in Eq. 6.216 of your textbook.

$$\text{Determine } T_c \text{ from: } N \equiv \int_0^\infty \frac{g(\varepsilon)}{e^{\beta_c(\varepsilon-\mu)}+1} d\varepsilon$$

$$\text{For } T < T_c, \; N = N_0 + \int_0^\infty \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1} d\varepsilon$$



5. Consider the van der Waals equation of states which is given in terms of scaled variables – pressure $\tilde{P} = P/P_c$, temperature $\tilde{T} = T/T_c$, and density $\tilde{\rho} = \rho/\rho_c$ (see Eq. 7.51):

$$\tilde{P} = \frac{8\tilde{\rho}\tilde{T}}{3-\tilde{\rho}} - 3(\tilde{\rho})^2. \tag{14}$$

For this same system, the dimensionless Gibb's free energy per particle function is given by Eq. 7.59.

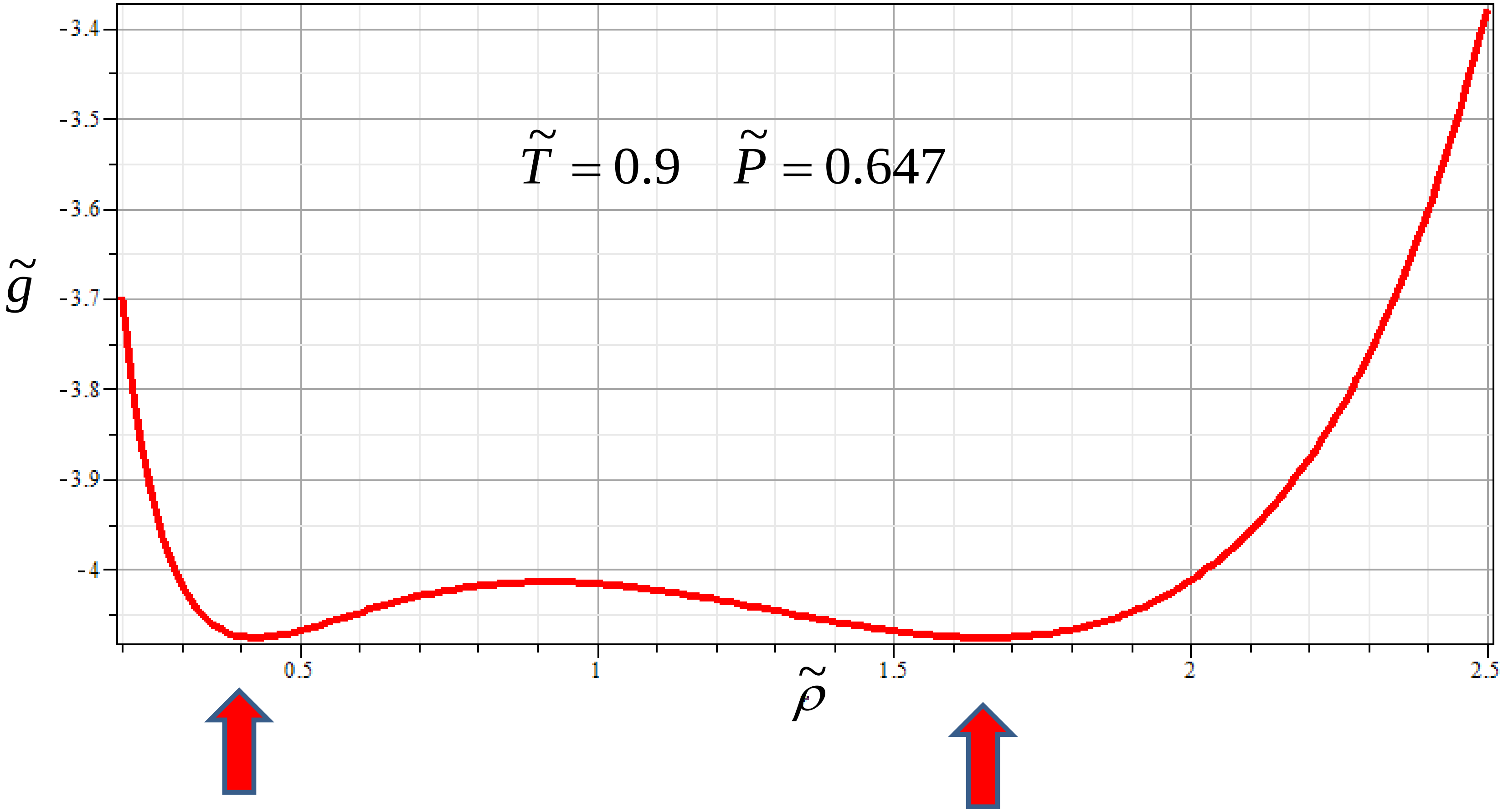
$$\tilde{g} = -3\tilde{\rho} - \frac{8}{3}\tilde{T}\ln\left(\frac{3}{\tilde{\rho}} - 1\right) + \frac{\tilde{P}}{\tilde{\rho}}. \tag{15}$$

(a) Your textbook shows that one point of fluid-vapor coexistence curve for this system is $[\tilde{T} = 0.9, \tilde{P} = 0.647]$. What are the corresponding values of the fluid and vapor densities $\tilde{\rho}_{\text{fluid}}$ and $\tilde{\rho}_{\text{vapor}}$.

(b) Find the corresponding coexistence parameters for $\tilde{T} = 0.8$.

See STP Chapt. 7 and Lecture Notes 28

Gibbs chemical potential at coexistence point



gas

liquid

Suggestions for efficient learning of topics covered on exam

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D. Other??

Resume discussion of virial coefficients:

Free energy for interacting particles :

$$F(T,V,N) = -kT\ln Z_N = -kT\ln Z_{IG} - kT\ln Z_C$$

$$= F_{IG}(V,V,N) + F_C(V,V,N)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V} - \left(\frac{\partial F_C}{\partial V}\right)_{T,N}$$

$$\frac{PV}{NkT} = 1 + \frac{V}{N}\left(\frac{\partial \ln Z_C}{\partial V}\right)_{T,N}$$

$$Z_C = \frac{1}{V^N}\int d^3r_1 d^3r_2 \cdots d^3r_N e^{-\beta U}$$

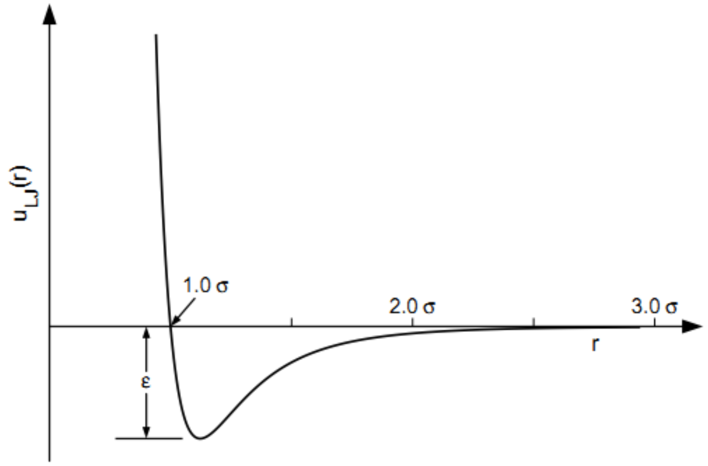
Model simulations of Z_c

Isotropic pairwise interaction potentials :

$$U(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N) = \sum_{i<j} u(|\mathbf{r}_1 - \mathbf{r}_2|)$$

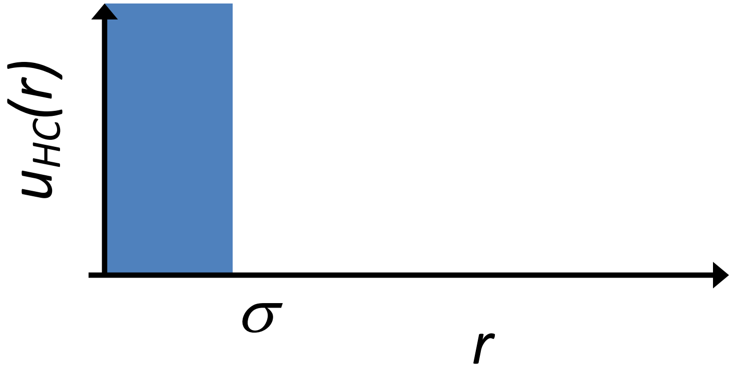
Lennard - Jones potential :

$$u_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Hard - core potential :

$$u_{HC}(r) = \begin{cases} \infty & \text{for } r < \sigma \\ 0 & \text{for } r < \sigma \end{cases}$$



For pair potential:

$$Z_C = \frac{1}{V^N}\int d^3r_1 d^3r_2 \cdots d^3r_N e^{-\beta U}$$

$$= \frac{1}{V^N}\int d^3r_1 d^3r_2 \cdots d^3r_N e^{-\beta u(r_{12})-\beta u(r_{23})-\beta u(r_{13})\cdots-\beta u(r_{(N-1)N})}$$

Define:

$$f_{ij} \equiv e^{-\beta u(r_{12})} - 1$$

$$Z_C = \frac{1}{V^N}\int d^3r_1 d^3r_2 \cdots d^3r_N (1+f_{12})(1+f_{23})(1+f_{13})\cdots(1+f_{(N-1)N})$$

$$= 1 + \frac{N(N-1)}{2V^2}\int d^3r_1 d^3r_2 f_{12} + \frac{N(N-1)(N-2)}{6V^3}\int d^3r_1 d^3r_2 d^3r_3 f_{12} f_{13} f_{23} \cdots$$

"Virial" expansion of equation of state:

$$\frac{PV}{NkT} = 1 + \frac{V}{N}\left(\frac{\partial \ln Z_C}{\partial V}\right)_{T,N}$$

$$\approx 1 + \rho B_2(T) + \rho^2 B_3(T) + \cdots$$

where $\rho \equiv \dfrac{N}{V}$

Evaluation of $B_2(T)$:

$$\frac{N(N-1)}{2V^2}\int d^3r_1 d^3r_2\, f_{12} = \frac{N(N-1)}{2V}\int d^3r_{12}\left(e^{-\beta u(r_{12})} - 1\right)$$

$$\left(\frac{\partial}{\partial V}\left(\frac{N(N-1)}{2V}\int d^3r_{12}\left(e^{-\beta u(r_{12})} - 1\right)\right)\right)_{T,N} \approx -\frac{\rho^2}{2}\int d^3r_{12}\left(e^{-\beta u(r_{12})} - 1\right)$$

$$\Rightarrow B_2(T) = -\frac{1}{2}\int d^3r_{12}\left(e^{-\beta u(r_{12})} - 1\right)$$

Evaluation of $B_2(T)$:

$$B_2(T) = -\frac{1}{2}\int d^3 r_{12}\left(e^{-\beta u(r_{12})} - 1\right)$$

For hard sphere: $B_2(T) = \dfrac{2\pi\sigma^3}{3}$

For square well: $B_2(T) = \dfrac{2\pi\sigma^3}{3}\left(1 - \left(e^{\beta\varepsilon} - 1\right)\left(R^3 - 1\right)\right)$

Lennard-Jones potential:

$$u_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$B_2(T) = -2\pi\sigma^3\int_0^\infty x^2 dx\left(e^{-4\varepsilon\beta\left(\frac{1}{x^{12}} - \frac{1}{x^6}\right)} - 1\right)$$